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CHEMISTRY

Extraction of Cesium-137 and Americium-241 by Calix[*n*]arenes from Carbonate-Alkaline Media[1]

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Abstract—Trends of cesium-137 and americium-241 extraction from carbonate–alkaline media with *p-tert*-butylcalix[*n*]arenes with macrocycles of different size ($n = 4, 6, 8$), including monofunctional derivatives with lipophilic substituents for increasing their solubility in organic media, were studied. It was demonstrated that *O-n*-octyl ethers of *p-tert*-butylcalix[6]arene appeared to be the most efficient extractants for Cs(I) cations, while it was *p-tert*-butylthiacalix[4]arene for and americium(III) cations.

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Currently, disposal of alkaline high-level waste, stored at the PA "Mayak," is considered an actual task. This waste with the volume of more than 18000 m^3 is presented by pulps containing sodium hydroxide, carbonate, nitrate, and nitrite in the presence of long-lived radionuclides: ^{137}Cs, ^{90}Sr, and transuranium elements [1].

Promising compounds for the extraction of long-lived radionuclides from alkaline media are calix- and thiacalixarenes—macrocyclic polyphenolic compounds [2]. The disadvantage of all studied calix[4]arenes is their low solubility in organic diluents and inability to extract cesium.

Simultaneous cesium and americium extraction from alkaline media is provided by *p-tert*-butylcalix[8]arene, but it is also low-soluble in organic diluents [3]. "Mixed" *p*-alkylcalix[8]arenes with different ratios of *tert*-butyl and isononyl groups at the upper rim of the calixarene platform appeared to be promising extractants [4]. The introduction of *iso*-nonyl groups instead of *tert*-butyl ones markedly increased the solubility of calixarenes in perchloroethylene (PCE), but significantly reduced the extraction efficiency of cesium and americium. Calix[8]arenes containing no more than two *iso*-nonyl groups in the calixarene platform, efficiently extract cesium and americium from alkaline media.

The introduction of alkyl and oxydiethylene glycol substituents into phenolic groups or bridging ethylene and diethylene glycol groups into the calix[8]arene molecule increases the efficiency of americium and cesium extraction from carbonate–alkaline media, simultaneously increasing the solubility of calixarenes in organic diluents. *tert*-Butylcalix[8]arene with a bridging diethylene glycol group extracts cesium most efficiently. For americium, the most efficient extractants were "mixed" *iso*-nonyl/*tert*-butyl(4/4)calix[8]arenes with bridging ethylene and diethylene glycol groups [5].

The aim of this work was to study patterns of cesium-137 and americium-241 extraction from carbonate–alkaline media with *p-tert*-butylcalix[n]arenes with macrocycles of different size ($n = 4, 6, 8$), including monofunctional derivatives with lipophilic substituents for enhancing calixarene solubility in low-polar organic media. In our study, perchloroethylene was used as a diluent, which simulates hexachlorobutadiene used in the radiochemical industry. Structural formulas of synthesized macrocycles are shown in Scheme 1. Macrocycles **I**-**V**, **VIII**, **IX** were obtained according to procedures, described in the literature [6–10].

Compound I, yield 37% (white powder), mp 155–158°C, ^1H NMR ($CDCl_3$) δ, ppm: 0.88 (t, $J = 7.1$ Hz, 3H, $-CH_3$), 1.17–1.62 (m, 46H: 36H, $-C(CH_3)_3$ + 10H, $-CH_2-$), 2.02–2.07 (m, 2H, $-CH_2-$), 4.26 (t,

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